THE SURFACE IONIZATION OF SALTS ON METALLIC FILAMENTS

BY

LYDA McCLELLEN ARNETT, JR.

B.S., West Virginia Wesleyan College, 1936
M.S., West Virginia University, 1938

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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Urbana, Illinois
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Introduction

Rodebush and Henry[1] were the first to observe the surface ionization of salts. They noted that positive ions are produced when alkali halide molecules strike an oxygen-coated tungsten filament. The ionization of potassium halides on clean tungsten and on oxygen-coated tungsten was investigated more thoroughly by Phipps and Copley[2] and by Hendricks, Phipps, and Copley.[3] These workers found that the ionization of the salt parallels that of the pure metal above 1600°K. This observation led them to apply the theory for the ionization of a metallic vapor surrounding a hot filament. This theory was developed by Langmuir and Kingdon[4] to treat their data for the ionization of cesium on tungsten.[6] According to this treatment, the ionization should obey the equation,

$$\frac{i_+}{i_a} = \frac{w_+}{w_a} \exp \frac{\Phi - I}{kT}$$

in which i_+/i_a is the ratio of ions to atoms evaporating from the filament, w_+ and w_a are the statistical weights of ions and atoms respectively, Φ is the Richardson work function of the surface, I is the work of ionization of the atom, k is Boltzmann's constant, and T is the absolute temperature of the filament. The fact that the ionization of the salt follows that of the pure metal above 1600°K indicated to these investigators that the salt probably dissociates into atoms before the ionization takes place. The ionization below 1600°K indicates that below this temperature a surface exists which has a work function higher than that of clean tungsten, probably caused by the adsorption of halogen atoms on a large fraction of the surface. Johnson and Phipps[6] studied the ionization of sodium halides on clean and oxygen-coated tungsten. Their results

substantiate the theory of the ionization of sodium atoms on tungsten when they take into account the presence of active spots on the tungsten which hold halogen atoms up to temperatures as high as 2600°K. The coverage necessary to bring their data into agreement with theory ranges from two to five percent depending upon the temperature of the filament and upon the halogen.

This investigation was undertaken to study the ionization of barium halides upon clean and oxygen-coated tungsten.

Experimental

A differential method was used in observing the positive ion currents from the filament in a beam of the salt. Two filaments, each surrounded by a cylindrical collector, were mounted parallel to each other and in the path of a salt beam originating from a 0.4mm. orifice in a platinum capsule surrounded by a heating element. This arrangement provided for the constancy of the ratio of beam intensities at the two filaments, independent of the absolute intensity of the beam. The ratio of the positive ion currents from the two filaments was measured by using variable resistances to adjust the fraction of each current which flowed through the respective halves of a center-tap galvanometer. This method employed the galvanometer as a null instrument. The variation of the positive ion current with filament temperature was measured by observing the ratios of the currents from the two filaments when one filament was kept at a constant temperature and the other one was set at various temperatures in the desired range.

The electron emission from the filament in the presence of the salt beam was also measured. During these measurements only one filament was employed and the galvanometer was used as a deflection instrument.

Results and Conclusions

No appreciable positive ion current was observed from barium chloride on tungsten below 1800°K. The positive ion

current increased more rapidly with temperature up to 2000°K than would be expected from the theory of the ionization of barium atoms on tungsten. From 2000°K to 2400°K the positive ion current increased less rapidly with increasing temperature than in the range 1800°K to 2000°K, in approximate agreement with theory. From 2400°K to 2600°K the positive ion current again increased rapidly with temperature.

The absence of appreciable ionization of barium chloride below 1800°K indicated a low work function surface below this temperature. In the study[6] of the ionization of sodium chloride on tungsten, it was observed that a high work function surface exists between 1300°K and 1600°K. The presence of the low work function surface with barium chloride on tungsten below 1800°K was also shown by the electron emission data. The electron emission from a barium chloride- covered filament at 1400°K is greater than the emission from a clean filament by a factor of 10^6. These data are used in support of the hypothesis that barium atoms remain adsorbed on a tungsten halogen surface and do not evaporate as ions below 1800°K. This tendency to remain adsorbed is overcome when the temperature 2000°K is reached and above this temperature the ionization follows approximately the theory of the ionization of barium atoms on tungsten. $I - \Phi$ was found to be about 0.10 electron-volt less in the temperature range 2000°K to 2400°K than that calculated from the known values. This is further evidence in support of the observation[6] that halogens remain adsorbed on active spots of the tungsten even to temperatures as high as 2600°K.

Three possible explanations for the increased positive ion currents above 2400°K have been considered. They are: (1) the onset of photo-electric currents; (2) the production of excited barium ions or doubly charged barium ions; and (3) the production of a surface with a work function less than that of clean tungsten above 2400°K. None of these explanations nor any combination of them serves to account for the increase to the extent that it is observed to occur.

The minimum electron emission from a tungsten filament covered with barium chloride was found to occur at about 1800°K, while the minimum emission from a filament covered with barium fluoride was found to occur at about 1870°K.

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VITA

The author was born May 26, 1916 at Piedmont, West Virginia. He attended the public schools of West Virginia, graduating from Spencer High School in May, 1932. In the fall of 1932, he entered West Virginia Wesleyan College and was in attendance for four years. He graduated as valedictorian in June, 1936 with the degree of B. S. Three years of service was rendered as an undergraduate assistant in chemistry. His education was continued for the next two years at West Virginia University from which institution he obtained the degree M. S. in chemistry in June, 1938. During these two years he served as an assistant in the Chemistry Department. In September, 1938 he entered the Graduate School of the University of Illinois. His work towards a graduate degree in Physical Chemistry continued in this institution to the present time. During the school year 1938-39 he served as an assistant in the Physical Chemistry Department. He was awarded University Fellowships for the two school years 1939-40 and 1940-41. He is a member of Sigma Xi, Phi Kappa Phi, and Phi Lambda Upsilon.

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